Investigation of the film thickness influence on the sensor response of In2O3-based sensors for O3 detection at low temperature and operando DRIFT study

proceedings

MDPI

Extended Abstract

Investigation of the Film Thickness Influence on the Sensor Response of In_2O_3-Based Sensors for O_3 Detection at Low Temperature and Operando DRIFT Study †

Daniele Ziegler [1,*], Paola Palmero [1], Jean-Marc Tulliani [1], Anna Staerz [2], Alexandru Oprea [2], Udo Weimar [2] and Nicolae Barsan [2]

[1] Politecnico di Torino, Department of Applied Science and Technology, INSTM R.U PoliTO-LINCE Laboratory, Corso Duca degli Abruzzi, 24, 10129 Torino, Italy; paola.palmero@polito.it (P.P.); jeanmarc.tulliani@polito.it (J.-M.T.)

[2] Institute of Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Auf der Morgenstelle 15, D-72076 Tuebingen, Germany; anna.staerz@ipc.uni-tuebingen.de (A.S.); alexandru.oprea@ipc.uni-tuebingen.de (A.O.); upw@ipc.uni-tuebingen.de (U.W.); nb@ipc.uni-tuebingen.de (N.B.)

* Correspondence: daniele.ziegler@polito.it

† Presented at the 8th GOSPEL Workshop. Gas Sensors Based on Semiconducting Metal Oxides: Basic Understanding & Application Fields, Ferrara, Italy, 20–21 June 2019.

Published: 19 June 2019

Industrial pollution and traffic emissions emit dangerous amounts of O_3, NO_2, VOCs and PM into environment, bringing higher incidence of morbidity and mortality in respiratory sicknesses [1]. Among tropospheric pollutant species, monitoring the O_3 concentration is remarkably important for its toxicity. The aftereffects of O_3 exposure indeed are upper respiratory irritation, rhinitis, cough, headache, occasional nausea, and vomiting [2]. In 2015, the United States Environmental Protection Agency (EPA), reinforced the National Ambient Air Quality Standards (NAAQS) for O_3 at ground-level not to exceed 70 ppb to improve the protection of human health [3].

This work presents n-type In_2O_3 as sensitive material to detect O_3 between 0.1 and 1 ppm at low temperatures (75 °C–150 °C). In_2O_3 powders were synthetized by hydrothermal route [4], with the goal to achieve a finer crystallite size, higher specific surface area and lower degree of agglomeration compared to commercial In_2O_3 (Sigma Aldrich, St. Louis, MO, USA). Those characteristics are essential to enhance the sensor performances [5].

In the synthesis, In_2O_3 nanostructures were realized by hydrothermal method using indium nitrate as indium precursor, soda as mineralizer and CTAB as capping agent, according to previous literature [6]. The mixture was maintained for 24 h at 70 °C and then for 12 h at 120 °C. Subsequently, powders were calcined at 400 °C for 30 min obtaining In_2O_3 [4].

In_2O_3 powders were characterized by laser granulometry, Thermal Analysis, X-ray Diffraction, N_2 adsorption, Field Emission-Scanning Electron Microscopy and High-Resolution Transmission Electron Microscopy.

Sensors were fabricated by screen-printing technique onto α-alumina substrates with Pt electrodes and a backside Pt heater. Inks for screen-printing were realized by mixing In_2O_3 powders with ethylene glycol monobutyral ether (Emflow), as organic vehicle and polyvinyl butyral (PVB) acting as temporary binder. After screen-printing deposition sensors were dried at 80 °C overnight and fired at 500 °C for 1 h in air. For obtaining different layer thicknesses in the range 10–100 μm, the first layer was dried and then a new layer was printed onto it.

Films were characterized by Scanning Electron Microscopy, electrical measurements and *operando* diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

Sensors were tested towards different amounts of O_3, NO_2 and H_2 under 0, 30% and 60% of RH (relative humidity) to study the selectivity of the as-realized chemical sensors for O_3 detection. Best results were achieved at 150 °C towards O_3, with the sensor selectivity for O_3 increasing by increasing the working temperature from 75 °C to 150 °C. Both oxidant gases (O_3 and NO_2) showed best performance at higher RH amounts, whereas for H_2 the trend was opposite, probably due to the competition between H_2 and H_2O for the same adsorption sites on the In_2O_3 surface. At 150 °C, under 1 ppm O_3, the variation of film resistance is 5 orders of magnitude, while it was only equal to 2 orders of magnitude under 1 ppm of NO_2. Under 30% RH, the influence of sensor thickness is much higher under O_3 compared to NO_2 and a logical trend was noticed in which by changing one order of magnitude the sensor thickness, the sensor response varies of more than 3 orders of magnitude under 1 ppm O_3. Under NO_2, only a small influence of the sensing film thickness on the sensor response was detected. Finally, the interference with H_2 is negligible as the sensor response towards H_2 is independent from the film thickness, as expected. Calibration curves of In_2O_3 sensor towards O_3, NO_2 and H_2 at 150 °C and 30% RH in the range 10–100 μm of thickness are displayed in Figure 1.

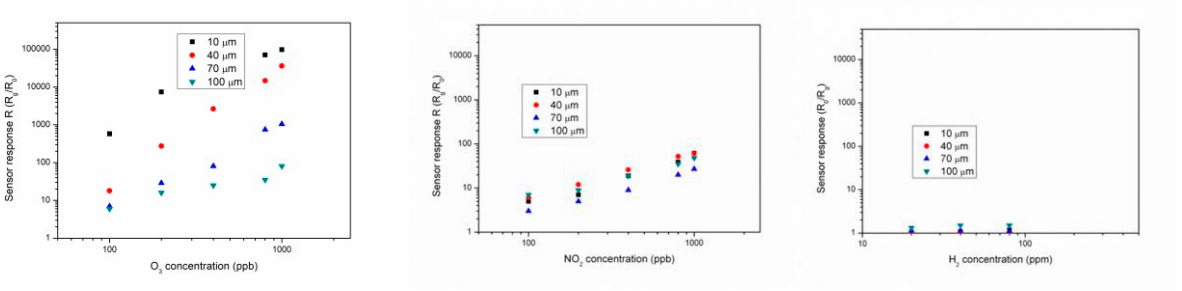

Figure 1. Comparison between 10, 40, 70 and 100 μm thick In_2O_3 sensor response towards O_3 (**left**), NO_2 (**center**) and H_2 (**right**) at 150 °C and 30% RH.

By DRIFTS, the aim is to clarify the interaction of NO_2 and O_3 with In_2O_3 surface establishing tightly the relationship between surface structure and adsorbed species with the gas sensing response.

Considering the NO_2-In_2O_3 interaction, the OH groups, most likely due to adsorbed water on the In_2O_3 surface, play a key role in the NO_2 adsorption. NO_2 withdraw more electrons from In_2O_3 in the presence of water forming nitrites and resulting in the measured increased in electrical resistance. This is confirmed by the higher increase in electrical resistance under humid atmospheres. OH groups are consumed when NO_2 is adsorbed onto the surface in the form of nitrites and in this process, H bonds are broken.

In the interaction of O_3 with In_2O_3 surface, signals related to peroxide formation during O_3 adsorption and decomposition were detected as well as peaks due to physisorbed O_3 still present at 150 °C. Furthermore, bands generated by carbonate-like species formed through reactions of O_3 with residual carbonaceous impurities from the synthesis route were recognized.

To conclude, in this work the role of the film thickness under O_3, NO_2 and H_2 exposure was studied for In_2O_3 sensor realized by screen printing technique. Finally, by operando DRIFT a complex sensing mechanism has been evidenced for In_2O_3 sensors, involving OH groups and adsorbed water in the mechanism of NO_2 adsorption and peroxide formation and O_3 physisorption during O_3 exposure.

References

1. Brunekreef, B.; Holgate, S.T. Air pollution and health. *Lancet* **2002**, *360*, 1233–1242, doi:10.1106/S0140-6736(02)11274-8.
2. Gottschalk, C.; Libra, J.A.; Saupe, A. *Ozonation of Water and Waste Water—A Practical Guide to Understanding Ozone and Its Applications*; Wiley: Weinheim, Germany, 2000.

3. 2015 National Ambient Air Quality Standards (NAAQS) for Ozone. Available online: https://www.epa.gov/ozone-pollution/2015-national-ambient-air-quality-standards-naaqs-ozone (accessed on 7 April 2019).
4. Shinde, D.V.; Ahn, D.Y.; Jadhav, V.V.; Lee, D.Y.; Shrestha, N.K.; Lee, J.K.; Lee, H.Y.; Maneb, R.S.; Han, S.H. A coordination chemistry approach for shape controlled synthesis of indium oxide nanostructures and their photoelectrochemical properties. *J. Mater. Chem. A* **2014**, 2, 5490–5498.
5. Korotcenkov, G.; Brinzari, V.; Cerneavschi, A.; Ivanov, M.; Golovanov, V.; Cornet, A.; Morante, J.; Cabot, A.; Arbiol, J. The influence of film structure on In_2O_3 gas response. *Thin Solid Films* **2004**, *460*, 315–323.
6. Yan, T.; Wang, X.; Long, J.; Liu, P.; Fu, X.; Zhang, G.; Fu, X. Urea-based hydrothermal growth, optical and photocatalytic properties of single-crystalline $In(OH)_3$ nanocubes. *J. Colloid Interface Sci.* **2008**, *325*, 425–431.